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NARMCO RESEARCH AND DEVELOPMENT
DIVISION OF NARMCO INDUSTRIES INC.
3540 AERO COURT, SAN DIEGO 11, CALIFORNIA
A SUBSIDIARY OF TELECOMPUTING CORPORATION

QUARTERLY PROGRESS REPORT NO. 3

RESEARCH AND DEVELOPMENT OF HIGH TEMPERATURE STRUCTURAL ADHESIVES

Contract No. NOw 61-0254-c

June 1961

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Quarterly Progress Report No. 3

Research and Development of High Temperature Structural Adhesives

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Narmco Industries, Inc.
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ABSTRACT

The report covers the work carried out during the period of 15 March 1961 to 15 June 1961.

Constructive pyrolysis of laminates at 1800°F in an argon atmosphere results in a major improvement in oxidation resistance when exposed to circulating air at either 650°F or 900°F. A silicone laminate, after this treatment, lost only 1.5% of its remaining resin content after 33 hours at 900°F. Despite the high pyrolysis temperature, the laminates retained a surprisingly large amount of their organic resin. Of further interest was the low resistivity after pyrolysis, ranging from 4 ohm-cm to 70 ohm-cm. The phenolic-181 E glass laminate had a room temperature flexural strength of just under 10,000 psi and a modulus of 5.4×10^6 psi. There is some indication that a chemical reaction occurs between E glass and the silicone resin.

The X-278-A adhesive had a tensile shear strength of 847 psi after two minutes at 1000°F, with a rapid heat up cycle of only one minute to simulate a missile temperature profile.

Mechanism studies on the sulfide curing compounds indicate that the type of epoxy polymerization is dependent upon the sulfur compound. Arsenic trisulfide appears to undergo a sulfur-oxirane oxygen exchange, as does thiourea and dithiocarbamate salts. Lewis salts of 2-mercaptobenzothiazole and stannic chloride promote a "regular" epoxy polymerization with the formation of hydroxyl groups.

Synthetic efforts have resulted in a polymer containing a -Si-O-Co- chain by reaction of cobalt acetate with a dialkoxysilane.

A polyketone was prepared by oxidation of polybenzyl, which was made via polymerization of benzyl alcohol.

Reaction of a nitrile rubber with hydroxylamine gave a polymeric amidoxine capable of reaction with Nickel ions.

Metal salts of 2-mercaptobenzothiazole were prepared and used to cure epoxy novolaks for mechanism studies and adhesive preparations.

The desired p-phenylene diarsonic acid was synthesized from arsanilic acid; this will be used in polymerization reactions of epoxies and to synthesize polymeric arsenic compounds.

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INTRODUCTION

The following progress was described in the second quarterly report under NOw 61-0254c:

1. A new adhesive, called X-278-A, was found to have unusual retention of tensile shear strength at 500°F on 17-7 stainless steel, after exposure to air at 500°F for 1000 hours. This adhesive also showed potential for either use at 900°F or for two minutes at 1000°F.

2. The initial experiments on pyrolysis of 181 glass fabric laminates, using standard resin systems, suggested that very substantial reduction in oxidation sensitivity can be achieved.

3. It was found that the free radical oxidation of diphenylmethane could be selectively inhibited by addition of polynuclear aromatic hydrocarbons.

4. An evaluation of bonding technique was carried out by using Metlbond 309 as the trial adhesive.

5. The synthesis of the 3,3'-dialdehyde of bisphenol-A was apparently accomplished in small yield. Further work on this compound, as an intermediate to chelate polymers, was discontinued.

DISCUSSION

1. CONSTRUCTIVE PYROLYSIS

The second quarterly report for NOw 61-0254-c, page 13, set forth the reasons for the start of this work. At that time, one pyrolysis was carried out using a Conolon 534 laminate (silicone-phenolic binder system). This work was repeated, using specimens from the same laminate, to determine the reproducibility of the entire process. It was found that after the 1000°F treatment the resin losses for both runs were 27.5% and 29.4%, while after the 1800°F treatment the total losses of resin were 33.1% and 35.3% for both determinations. These represent fairly close checks and were considered satisfactory.

Figure 1 is a plot of oxidation weight loss when an untreated control was heated in circulating air at 650°F along with the specimens pyrolyzed at 1000°F and 1800°F. Once again, the total weight changes were within satisfactory limits. The control lost 19% and 18%, the 1000°F specimen lost 65% and 62%, while the 1800°F specimen lost 8% and 6.5%. Further work on this treatment went on with a higher degree of confidence in the results because of the satisfactory precision and because it verified the poor oxidation resistance of the specimen heated to 1000°F. It was anticipated that this treatment would give oxidation resistance between that of the control and the 1800°F specimen. It will be seen in the other pyrolysis data that in one system the 1000°F specimen was better than the control. As a result of the duplicate runs, this reversal is believed to be genuine.

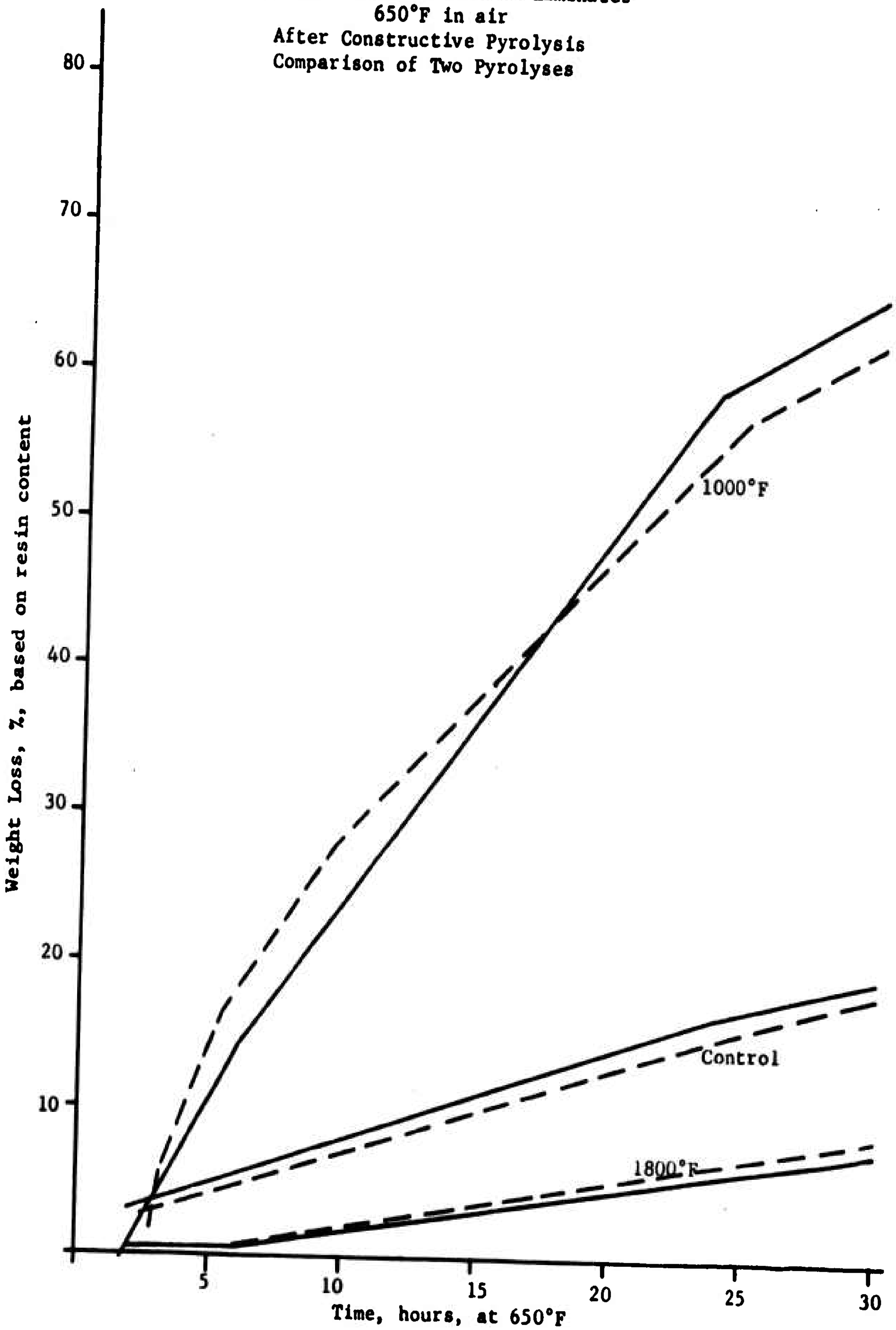
The second pyrolysis, with the Conolon 534 laminates on E glass, was also used to collect room temperature flexural strength and modulus. These data were:

	Flexural Strength psi	Modulus x 10^6 psi
Control	94,760	4.54
1000°F	11,290	2.64
1800°F	9,180	5.23

It can be seen that the 1000°F pyrolysis caused the major decrease in flexural strength while decreasing the modulus by almost 50%; the 1800°F specimen, while suffering some further decrease in flexural strength, had double the modulus of the 1000°F specimen and 20% more than the control. Examination of the specimens under a microscope showed that the 1800°F pyrolysis resulted in a dense resin phase while the 1000°F specimen showed its porous nature. It seems fairly certain that the greatly increased oxidation rate in the 1000°F specimen was at least partially due to this

Figure 1

Weight Loss
Silicone-Phenolic E-Glass Laminates
650°F in air
After Constructive Pyrolysis
Comparison of Two Pyrolyses



porosity. Yet this apparently is not the only reason, because in the silicone laminates, to be discussed later, such porosity was absent but the oxidation rate was still much more rapid. It would appear that the 1000°F pyrolysis left a resin phase which was more highly reactive because of some unknown molecular structural changes.

At this point, it should be mentioned that despite the 1800°F treatment in argon, the total loss of resin was only about a third. This is considered to be small for such an exposure temperature and indicative that if oxidative degradation could be avoided, certain organic polymers already have the necessary thermal stability. With one exception, all representative binder systems exhibited this resistance to thermal energy.

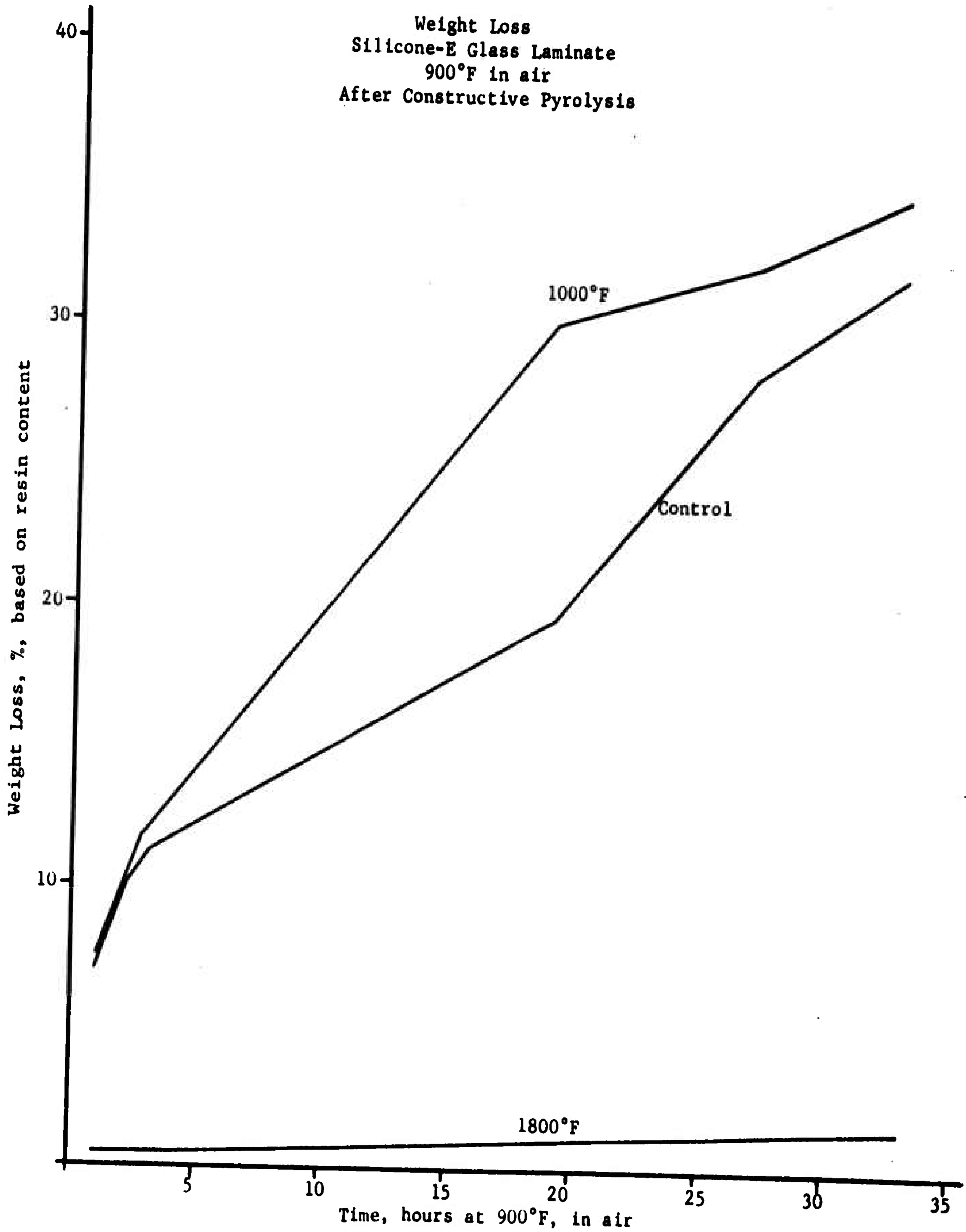
Microscopic examination of this silicone-phenolic system, after pyrolysis, showed that some of the glass had melted along the cut edges, but not at the flat sides. This also took place with the pure silicone laminates, but to such an extent to be seen on all sides and to produce a large degree of shrinkage. However, those laminates constructed with binder systems free of silicone resins, failed to show any molten glass or shrinkage. It is believed, at present, that reaction between the glass and the silicone resin produces a lower melting glass.

The small amount of liquid condensate from the silicone-phenolic pyrolysis was dissolved in ether and removed from the dry-ice trap. Water was present in addition to an organic phase. Infra-red analysis showed that the organic material contained hydroxyl and carbonyl groups. The carbonyl group could have arisen by formation of a quinone-methide during pyrolysis, which then reacted with water to yield an aldehyde.

A laminate made of E glass and a silicone resin was pyrolyzed and found to have lost 6.4% of its resin after the 1000°F treatment and 21.1% after pyrolysis at 1800°F, indicating greater thermal stability than in the silicone-phenolic. Specimens, plus a control, were then exposed to air at 900°F to determine the oxidative weight loss. Here, the control lost 31.8%, the 1000°F specimen lost 34.5%, while the 1800°F specimen lost 1.6%, all after 33 hours exposure. See Figure 2. The 1800°F specimen showed a considerable amount of molten glass and had shrunk 17.5% in length and 15.6% in width. It appeared that the greater amount of molten glass found in the pure silicone laminate was due to the opportunity for more reaction between the silicone resin and the glass.

Another interesting phenomenon was noticed after the 33 hour exposure to air at 900°F. Both the control and 1000°F specimen showed the typical degradation of the glass carrier, which was now extremely weak and friable. The 1800°F specimen was still extremely strong and, except for signs of melting, appeared to be unchanged. This suggested that air is necessary for the degradation of E glass, when heated in a silicone resin matrix.

Figure 2



Weight Loss
Silicone-E Glass Laminate
900°F in air
After Constructive Pyrolysis
40
30
20
10
Weight Loss, %, based on resin content
1000°F
Control
1800°F
5
10
15
20
25
30
35
Time, hours at 900°F, in air

The resistivity of the specimens were measured with an ohm-meter. While the unpyrolyzed silicone control had infinite resistivity, the 1000°F and 1800°F specimens gave values of 70 ohm-cm and 61 ohm-cm, respectively, thus placing them in the semi-conductor area. The ability to conduct a current is related to the mobility of electrons. Such mobility is found in polynuclear condensed ring systems which have π electron clouds capable of moving from one ring to another (resonance stabilization). The low resistivity can be considered an indication that the pyrolysis produced such a polymer. While graphite is also a good conductor, the pyrolysis temperature is considerably lower than graphitization temperatures.

A high temperature epoxy laminate, using Epon 828 and m-phenylenediamine, was subjected to pyrolysis at 1000°F. A large amount of liquid condensate resulted and it was found that the laminate lost 76% of its original resin content. This showed that the epoxy polymer was considerably less thermally stable than any of the binder systems that were pyrolyzed. Because of this drastic degradation in argon, pyrolytic exposure to 1800°F followed by exposure to air was omitted.

A laminate was prepared from an epoxy-novolak cured with methyl nadic anhydride and DMP-30. Upon pyrolysis at 1000°F and 1800°F, this showed a resin loss of 45.4% and 47.3%, respectively. After 30 hours at 650°F, the unpyrolyzed control lost 51.4%, the 1000°F specimen lost 35.8%, and the 1800°F sample lost only 3.4%. There was no evidence of molten glass in the 1800°F specimen. See Figure 3.

A pure phenolic laminate was made from Conolon 5141 and subjected to the pyrolytic treatment. After the 1000°F and 1800°F exposures in argon, the resin losses were identical, 31.8%. This was interesting, because now both the specimens, upon exposure to circulating air at 650°F, had identical resin content, and any differences in oxidation must be due to differences in the structure on the remaining organic material. The following physical properties were found at room temperature:

	Flexural Strength psi	Modulus $\times 10^6$ psi
Control	69,620	3.5
1000°F	15,850	2.4
1800°F	9,980	5.4

Once again the 1800°F sample showed a significant increase in modulus over the other specimens. The flexural strength of almost 10,000 psi was encouraging, because it was not too far from an acceptable design strength. It is an immediate objective to achieve superior oxidation resistance with a flexural strength of 15,000 psi.

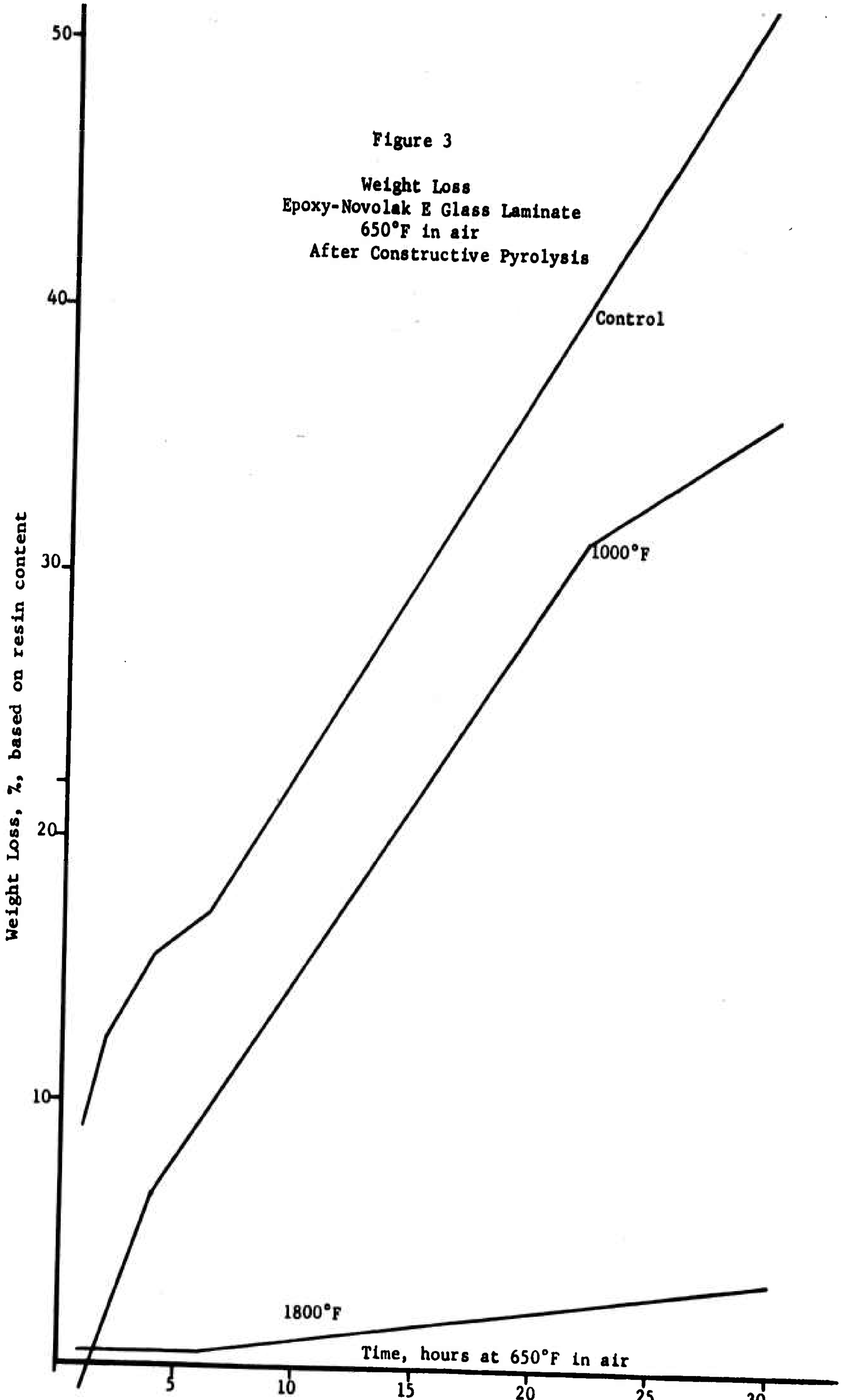


Figure 3
Weight Loss
Epoxy-Novolak E Glass Laminate
650°F in air
After Constructive Pyrolysis
Control
1000°F
1800°F
Weight Loss, %, based on resin content
Time, hours at 650°F in air
50
40
30
20
10
5
10
15
20
25
30

On exposure to circulating air at 650°F for 30 hours, the control lost 51%, the 1000°F specimen lost 76%, and the 1800°F sample lost only 8.6%. See Figure 4. There was no shrinkage or signs of molten glass in the 1800°F specimen.

These pyrolyses again indicated an order of purely thermal stability, which agreed with the order found in adhesives and laminates. This was silicone $>$ phenolic $>$ silicone-phenolic $>$ epoxy-novolak $\gg$ epoxy.

The high order of oxidation stability found in the pyrolyzed silicone was most encouraging. However, to achieve higher flexural strengths, some carrier other than E glass would have to be used because the 1800°F exposure caused a marked decrease in strength of the glass. Accordingly, a laminate was made from the same silicone resin on quartz fabric and subjected to the pyrolytic treatment. The specimens lost 15% and 19.1% after exposure to 1000°F and 1800°F, respectively. Physical testing at room temperature gave the following data:

	Flexural Strength psi	Modulus $\times 10^6$ psi
Control	28,660	2.53
1000°F	4,570	2.04
1800°F	2,930	3.01

These data were most disappointing because of the poor flexural and modulus values. Weaker flexural values were anticipated in the control because of past experience with quartz fabric. However, it was reasonable to expect the quartz to maintain its strength better than E glass at elevated temperatures. After the 1800°F treatment there was no evidence of molten fabric when viewed under the microscope. For the weight loss study at 900°F in air, see Figure 5.

The marked difference in behavior between E glass and quartz is worth further comments. Why was the E glass melted at 1800°F and the quartz unaffected when both were in a silicone matrix? It is believed that a chemical reaction took place with the E glass; the silicone resin could have reacted with the E glass to form a lower melting glassy composition. Further, evidence of a possible chemical reaction is found in the resistivity of the pyrolyzed quartz laminates. The 1000°F and 1800°F specimens had resistivities of infinity and 1.9×10^6 ohm-cm respectively, as compared to 70 ohm-cm and 61 ohm-cm. E glass contains B_2O_3, Al_2O_3 and CaO, while quartz is pure SiO_2. It is possible that the low resistivity in E glass laminates is due to a reaction to give a polymer containing calcium, boron, or aluminum, while the quartz would not form any new materials. The presence of calcium and boron could contribute to conductivity, especially calcium.

Figure 4

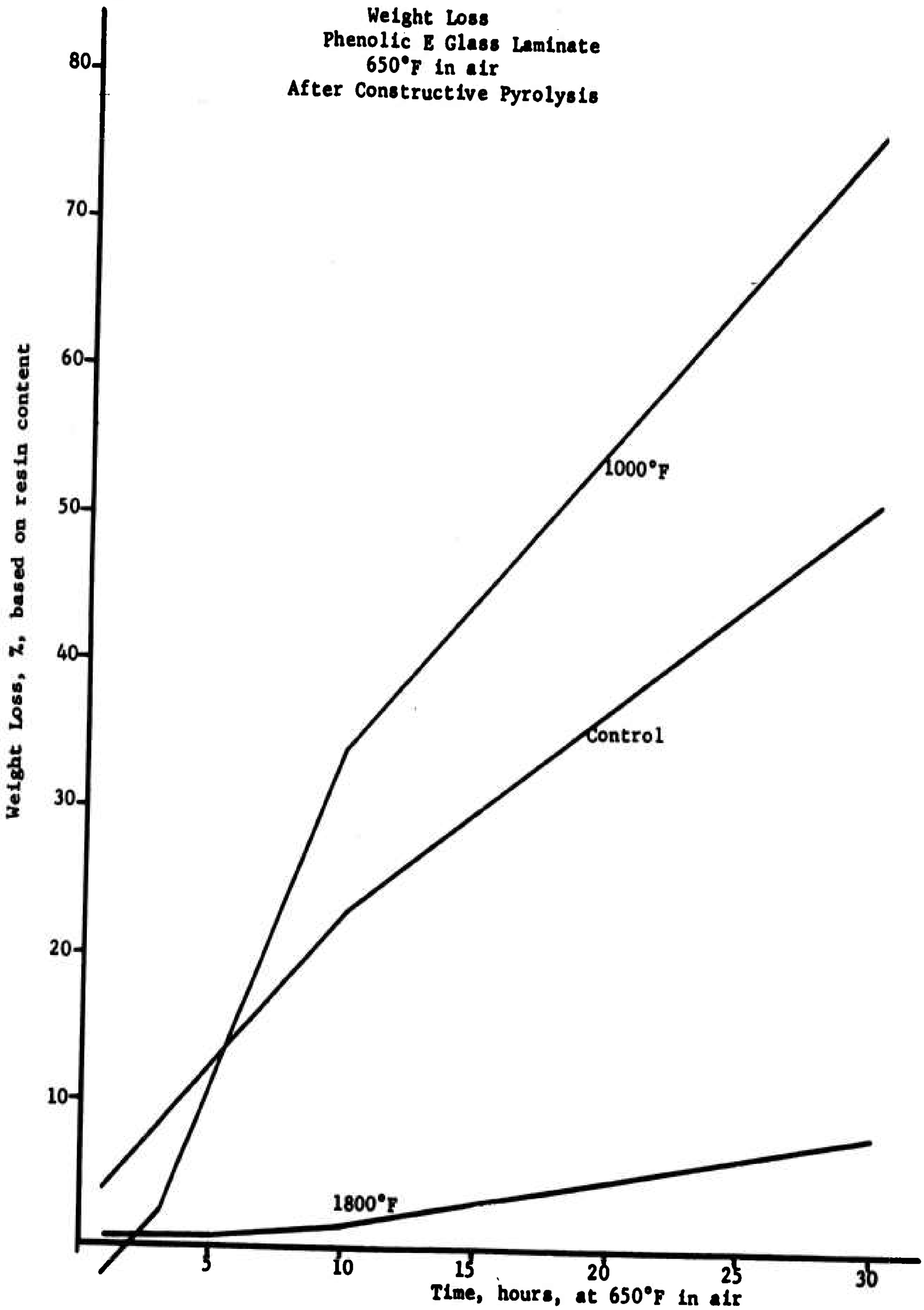
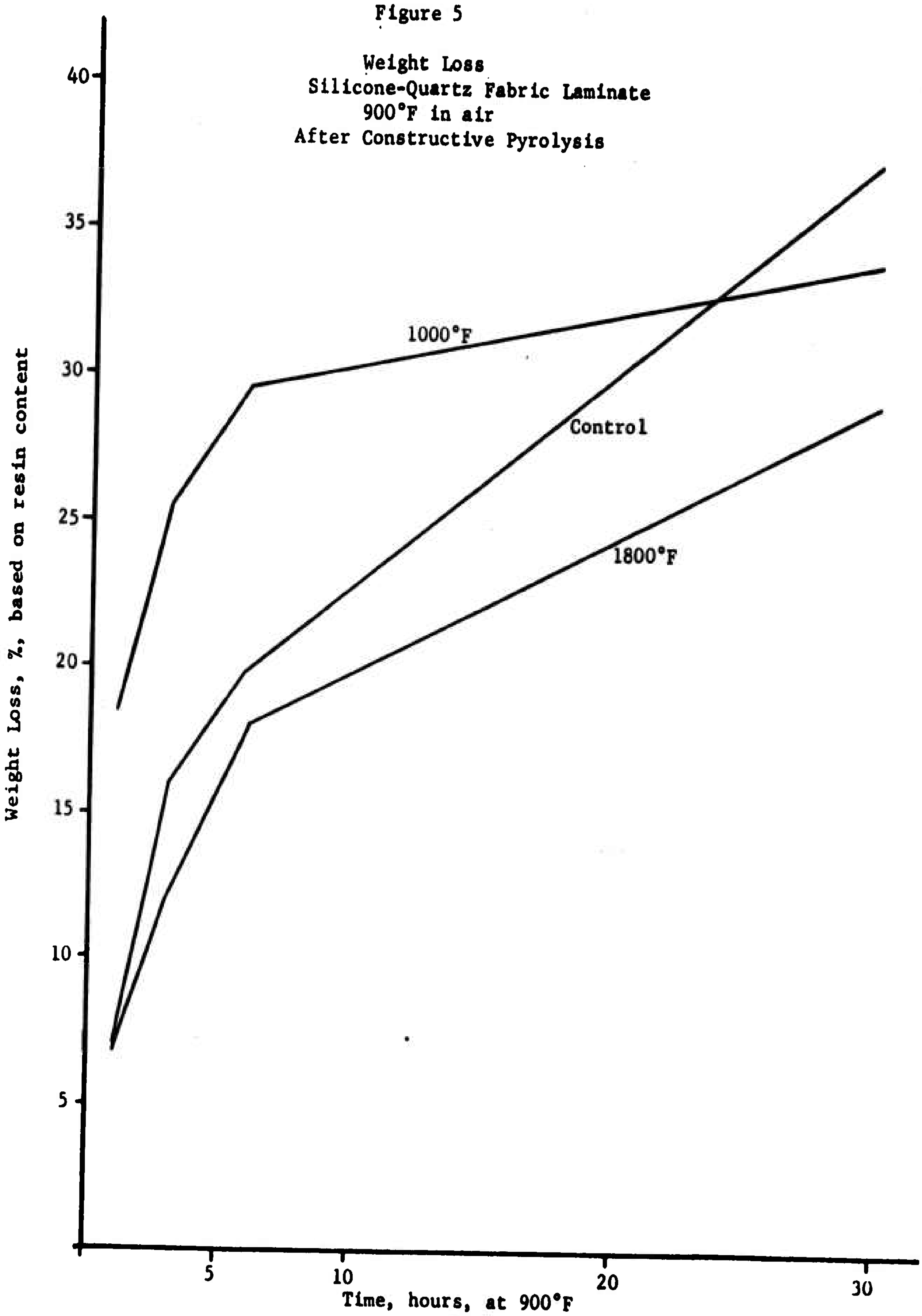

Weight Loss
Phenolic E Glass Laminate
650°F in air
After Constructive Pyrolysis
80
70
60
50
40
30
20
10
Weight Loss, %, based on resin content
1000°F
Control
1800°F
5
10
15
20
25
30
Time, hours, at 650°F in air

Figure 5

Weight Loss
Silicone-Quartz Fabric Laminate
900°F in air
After Constructive Pyrolysis



If this reaction took place, it is potentially a new method for synthesizing semi-inorganic polymers with very high oxidation resistance. This shall be carried out in the near future. Another possible application for such a reaction product could be as a conductive glass.

2. ADHESIVES

Work with the Metlbond 309 system was continued and data collected after two minutes at 1000°F. Quartz lamps were used to attain temperature in one minute. By such a test method, the temperature profile more closely approximated conditions found in a missile. Tensile shear strengths of 600-700 psi were obtained.

The use of polymeric titanium dioxide as a steel prime or fiber glass carrier finish failed to provide any benefit. When the isopropyl-ortho-titanate was replaced by isopropylantimonite, poorer values were obtained. The use of magnesium methoxide to form magnesium oxide resulted in virtually complete loss of adhesion under all test conditions.

The X-278 adhesive gave from 500 to 650 psi in tensile shear after two minutes at 1000°F, while an adhesive based on Resinox SC-1008 gave 835 psi.

Mechanism studies on the role of sulfur compounds showed that certain rubber accelerators were capable of curing the epoxy novolak. Dithio-oxamide gave an extremely brittle adhesive with very poor properties over the entire temperature range. Ethyl zimate (zinc diethyldithiocarbamate) was so active a curing agent that some difficulty was experienced in preventing destructive exotherms during curing. However, poor data were obtained under all test conditions except at room temperature, which gave 3045 psi.

The X-278-A system received some further investigation and gave 847 psi after two minutes at 1000°F. Addition of the highly active tin salt of 2-mercaptobenzothiazole caused a slight decrease in properties at all test conditions. It was hoped that this highly active salt would permit a reduction in the 600°F curing temperature, but lower values also resulted.

3. MECHANISMS

The second quarterly report mentioned the start of the study to learn the reaction between arsenic trisulfide and the epoxy-novolak. As was done with the mechanism study on arsenic pentoxide, phenylglycidyl ether was selected as a model compound.

Interaction of arsenic trisulfide and phenylglycidyl ether occurred at 135°C when the trisulfide suddenly dissolved, almost immediately an exothermic reaction set in. After further heating and stirring, a white precipitate formed. Subsequent infrared analysis showed this solid to be arsenic trioxide.

Distillation of the reaction mixture gave an unknown carbonyl compound, phenol and fractions possessing sulfury odors. Infrared analysis showed the disappearance of the epoxy absorptions and the appearance of a strong hydroxyl absorption. This showed a major difference from the reaction of arsenic pentoxide, which promoted polyethers rather than the usual epoxy polymers containing hydroxyl groups; arsenic trisulfide did not form polyethers, but did form the usual polyhydroxyl-polyether.

The formation of arsenic trioxide from the arsenic trisulfide was also interesting because it suggested an oxygen-sulfur exchange. Which oxygen atom is replaced by sulfur is not known, although it is believed to be the oxirane oxygen

$$-O-CH_2-\underbrace{CH-CH_2}_{O} + As_2S_3 \longrightarrow -O-CH_2-\underbrace{CH-CH_2}_{S} + As_2O_3$$

because this is the most active oxygen atom in the molecule. The cyclic sulfur compounds, called thiiranes, are extremely susceptible to either acid or base catalysis, leading to polymerization.

Formation of phenol would have to come from the phenylglycidyl ether. Yet, it appears unlikely that the ether linkage was ruptured as follows

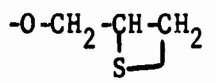
$$\emptyset-O-CH_2-\underbrace{CH-CH_2}_{O} \xrightarrow{H_2O} \emptyset-OH + HO-CH_2-\underbrace{CH-CH_2}_{O}$$

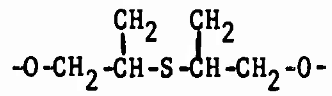
to give phenol and glycidol. Glycidol is highly reactive and would either polymerize or react with phenol to give $\emptyset-O-CH_2-\underset{OH}{CH}-CH_2-OH$.

During the course of this experiment, sulfur absorptions were completely absent in the infrared spectrum. Apparently, these absorptions are beyond the 15 μ limit of the instrument. A spectrum of arsenic trisulfide showed its complete transparency. It is unfortunate that the infrared spectrophotometer cannot play its useful part in this work.

Another reaction was carried out, but this time under nitrogen. It seemed reasonable that arsenic trisulfide could be oxidized by air at a reaction temperature up to 200°C. However, it was found that arsenic trioxide was again formed and this gave weight to the idea of an oxirane oxygen-sulfur exchange.

If the thiirane moiety was formed on reaction, this would lead to thioether formation





The thioether linkage is found between 3-15 μ but it does absorb weakly. However, the sulfone $-SO_2-$ group has a fairly strong absorption. Some of the polymeric residue was dissolved in glacial acetic acid and heated with 30% hydrogen peroxide. A spectrum, after work-up, showed a new medium peak at 8.90-8.95 μ and a shoulder that developed at 7.65 μ. The sulfone group has been assigned absorptions at 7.41-7.69 μ (s) and 8.62-8.93 μ (s). Although the spectrum was complex, this indicates the strong possibility of the thioether linkage in the polymer.

The polymeric residue from the distillation was stripped of volatiles at 0.1 mm up to 200°C and subjected to thermogravimetric analysis. Up to 250°F there was no weight loss, while from 550°F to 650°F the substance lost 62% of its weight. The complete lack of oxidation up to 550°F is in line with the stability of X-278-A, which showed good strength retention up to 1000 hours at 500°F. See Figure 6.

A reaction with diphenyldiethoxysilane and arsenic trisulfide was run, but since no changes were found in the spectrum the reaction mixture was discarded. In the light of what was found with sulfur absorptions with phenylglycidyl ether, the reaction should be repeated and completely worked up chemically.

Work on the mechanism was broadened to include thiourea. Reaction with phenylglycidyl ether resulted in the formation of urea, which was isolated and identified by mixed melting point and infrared spectrum.

Fractional distillation gave only small quantities of distillates boiling at 56°C/4.5 mm (3.68 g), and 76°C/2.00 mm (3.28 g). There was 1.12 g found in the dry-ice trap. All three fractions gave negative carbonyl tests. The distillation residue was found to contain sulfur, as shown by sodium fusion. Heating the distillation residue with strong caustic gave vapors which were basic, indicating amino or amide nitrogen (of course, this could be from urea or thiourea as well as some reaction product).

Infrared examination of the distillation residue, when compared to phenylglycidyl ether, showed a OH and/or NH absorption at 2.9-3.2 μ, an absorption at 5.8 μ, which was believed to be due to $-\overset{O}{C}NH-$ from urea, and a weak peak at 7.35 μ, which could be due to the -C=S group from thiourea. Further, all epoxy absorptions were completely gone. The material boiling at 56°/4.5 mm also showed absorptions at 2.9-3.2 μ and 7.4 μ, while the epoxy absorptions were decreased and the 5.8 μ peak was missing. The higher boiling distillate contained the 5.8 μ peak and epoxy peaks.

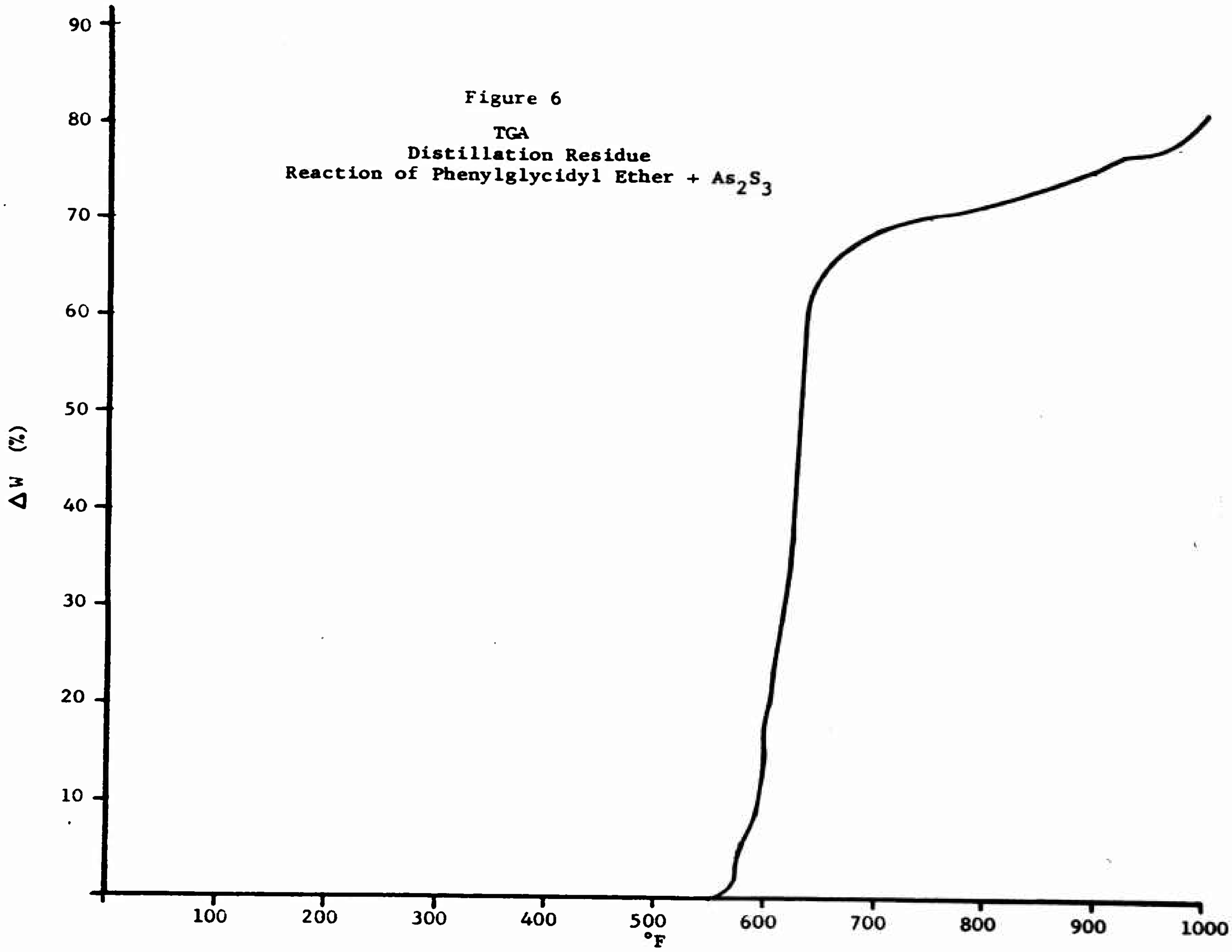


Figure 6

TGA
Distillation Residue
Reaction of Phenylglycidyl Ether + As_2S_3

Reaction of an epoxy-novolak with a rubber accelerator, ethyl zimate [zinc diethyldithio carbamate-$Et_2NC(S)S\ ZnSC(S)NEt_2$], proceeded so vigorously that careful control had to be maintained. The reaction mixture was compared with a mixture of the reactants, prior to heating, and showed new absorptions at 5.95 μ and 6.10 μ, which are due to -C$\overset{O}{-}$N- groups. Of great interest is the fact that the -OH and/or -NH- peak at about 3.0 μ failed to appear. Since the resin increased in viscosity, it would be reasonable to assume reaction of the epoxy group, which should lead to an absorption at 3.0 μ.

Thus, it might be reasoned that the reaction led to an exchange of sulfur for epoxy oxygen and, on further reaction, the thioether linkage was formed; thus the lack of an OH absorption. Another possibility is that the epoxy compound polymerized to form a polyether, in which case the hydroxyl groups would be terminal groups and not show increased absorption at 3.0 μ. Of course, both reactions could take place simultaneously.

Regardless of how the epoxy group reacted, a decrease in its absorption at 10.95-11.00 μ was anticipated but not found. This was explained by the spectrum of the ethyl zimate, which absorbed strongly in this region, thus masking the disappearance of the epoxy group.

Reaction of the epoxy novolak with the bismuth and nickel salts of diethyldithiocarbamic acid gave the same changes in the infrared spectra as with the zinc salt. However, the reaction of the stannic salt of 2-mercaptobenzothiazole gave a spectrum with strong absorption at 2.95 μ, indicating hydroxyl group formation along with a decrease in epoxy absorptions. In addition, carbonyl absorptions appeared again at 5.95-6.10 μ.

It appears that the type of polymerization is dependent upon the curing agent used. There is reason to believe (see later) that the stannic salt of 2-mercaptobenzothiazole consists of a coordination bond between Sn and the ring N (Lewis Salt) rather than as the $-(S)_4Sn$ salt. Yet, it would be anticipated that a Lewis salt should form OH groups in the same way that $BF_3.EtNH_2$ does in standard curing reactions.

4. SYNTHESIS

a. Benzyl alcohol was polymerized with concentrated sulfuric acid to give polybenzyl[1], m.p. 56-63°C. This in turn was oxidized with nitric acid to yield a polyketone, m.p. 120-130°C[1]. The infrared spectrum indicated the possibility of some dicarboxylic acid formation. After treatment with aqueous sodium carbonate, the carbonyl absorptions

(1) Shriner and Birger J. Org. Chem. 6 305 (1941).

remained, but a decrease in the OH absorption was noticed. More of the polyketone and polybenzyl will be prepared to study the oxidation of the hydrocarbon (as was done with diphenylmethane) to determine the heat stability of the polyketone and for possible conversion of the linkages to $-CF_2-$ linkages.

b. Arsanilic acid was diazotized and converted to p-phenylene diarsonic acid. The method of Dr. Hobin of Great Britain was used at the suggestion of Dr. Porter W. Erickson. This material was unmelted at 405°C, with slight darkening at 380°C. This compound will be evaluated as a curing agent and for possible conversion to the p-phenylene tetrahalo diarsine, to be used to prepare arsenic polymers.

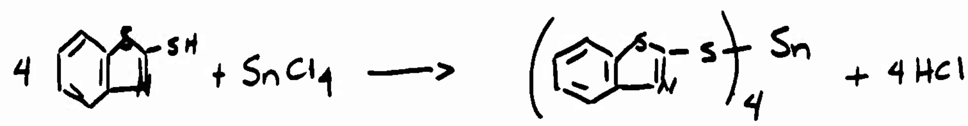
Heating the diarsonic acid with an epoxy novolak to 320°F failed to cause any polymerization. Since the diarsonic acid has two strong protons (K_1 = about 10^{-3}), the failure to react could be due to the insolubility of the compound.

c. Diphenylsilanediol and activated aluminum were heated to 245°C without any substantial signs of reaction.

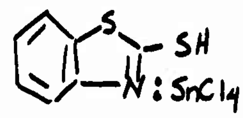
d. Reaction of B,B',B"-trichloroborazole and glycidol gave a very hygroscopic white solid, m.p. 85-90°C (decomp.), which gave a positive chloride test in water. Apparently the reaction product was extremely sensitive to moisture and this could be due to B-O-C bonds.

e. The zinc salt of 2-mercaptobenzothiazole was synthesized by reaction of zinc chloride with an aqueous solution of the sodium salt of 2-mercaptobenzothiazole.

f. Reaction of 2-mercaptobenzothiazole was carried out with antimony pentachloride in carbon tetrachloride. The use of the aqueous sodium salt was not tried because of hydrolysis of the halide compound. In an analagous manner, the stannic salt was also prepared. During this reaction the condenser was connected to a solution of standard sodium hydroxide. There was no evolution of hydrogen chloride. The anticipated reaction failed to occur:

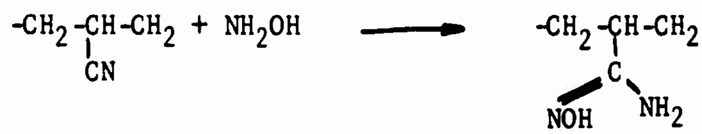


Instead, the reaction product, which was a bright yellow precipitate, is believed to be a Lewis Salt in which the $SnCl_4$ reacted as a Lewis acid, with the ring nitrogen acting as the Lewis base to give



The product was dissolved in dilute aqueous alkali acidified with nitric acid and added to silver nitrate to give a white precipitate of silver chloride. This, of course, indicated the Lewis Salt structure. The fact that this compound was soluble in dilute alkali was indication of free -SH- groups.

g. An attempt was made to prepare a chelate polymer by another route. This involved reaction of a nitrile rubber with hydroxylamine to form amidoxine groups



which should be capable of chelation. After the reaction, a large decrease was found in the nitrile absorption at 4.5μ while the C=N- bonding absorption appeared as a strong peak at 6.2-6.6μ. Reaction of the product gave a precipitate with Ni^{++} but apparently failed with Co^{++} and Cu^{++}.

h. Interaction of anhydrous cobalt acetate with phenylmethyldiethoxysilane was carried out to give a blue-gray solid and ethyl acetate. The solid was unmelted at 405°C and was apparently quite stable in boiling water. Analysis showed 25.2% Co and 15.8% silicon; theory is 28.0% Co and 13.25% Si. The high silicon and low cobalt values could be due to partial polymerization through Si-O-Si linkages. Infrared analysis showed Si-O- and Si-phenyl linkages. TGA showed a weight loss of 42.1% at 1000°F and the main degradation at 650°-825°F. See Figures 7 and 8.

Figure 7

TGA
Polymer from XR-820 + $Co(Ac)_2$

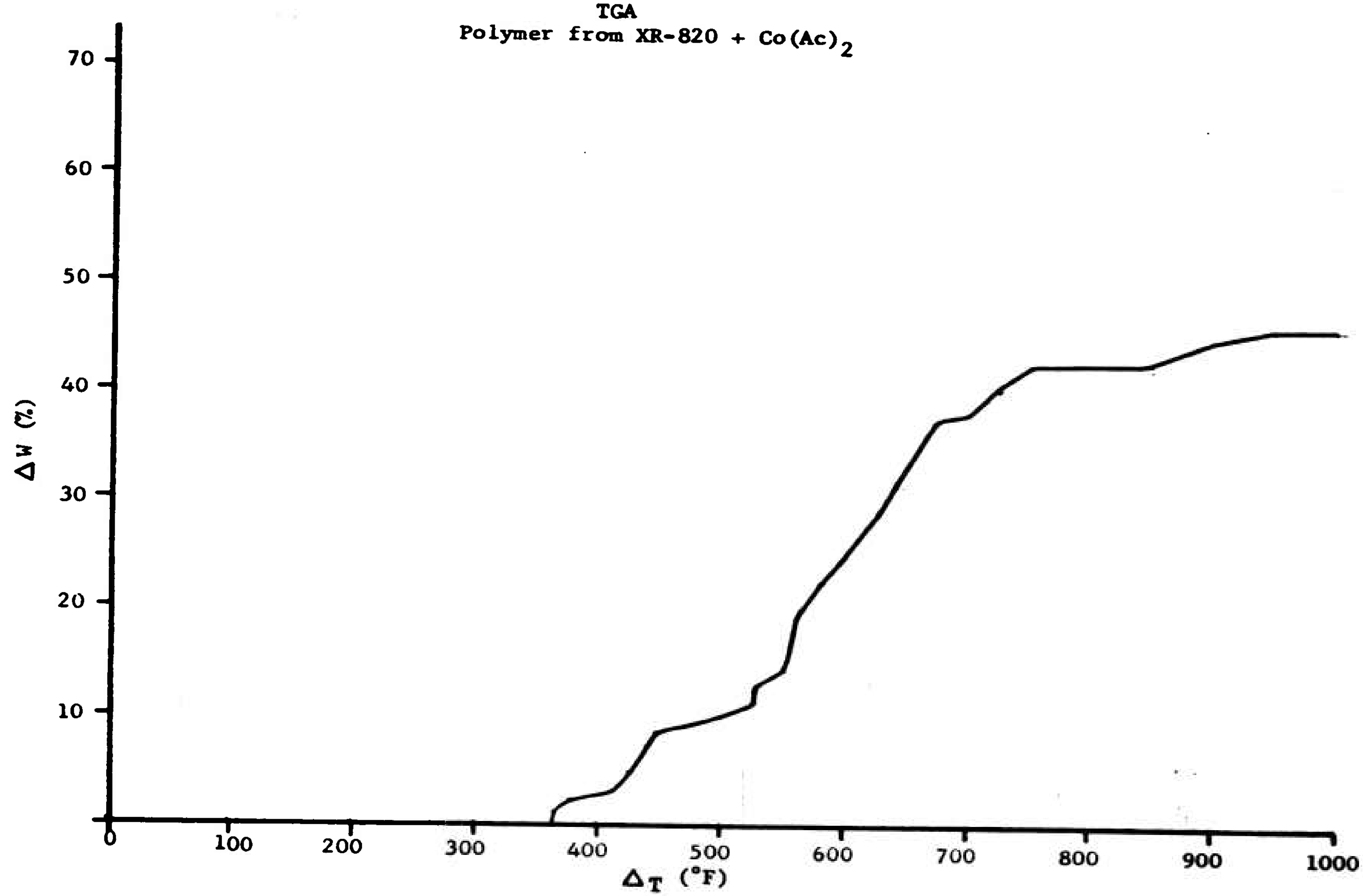
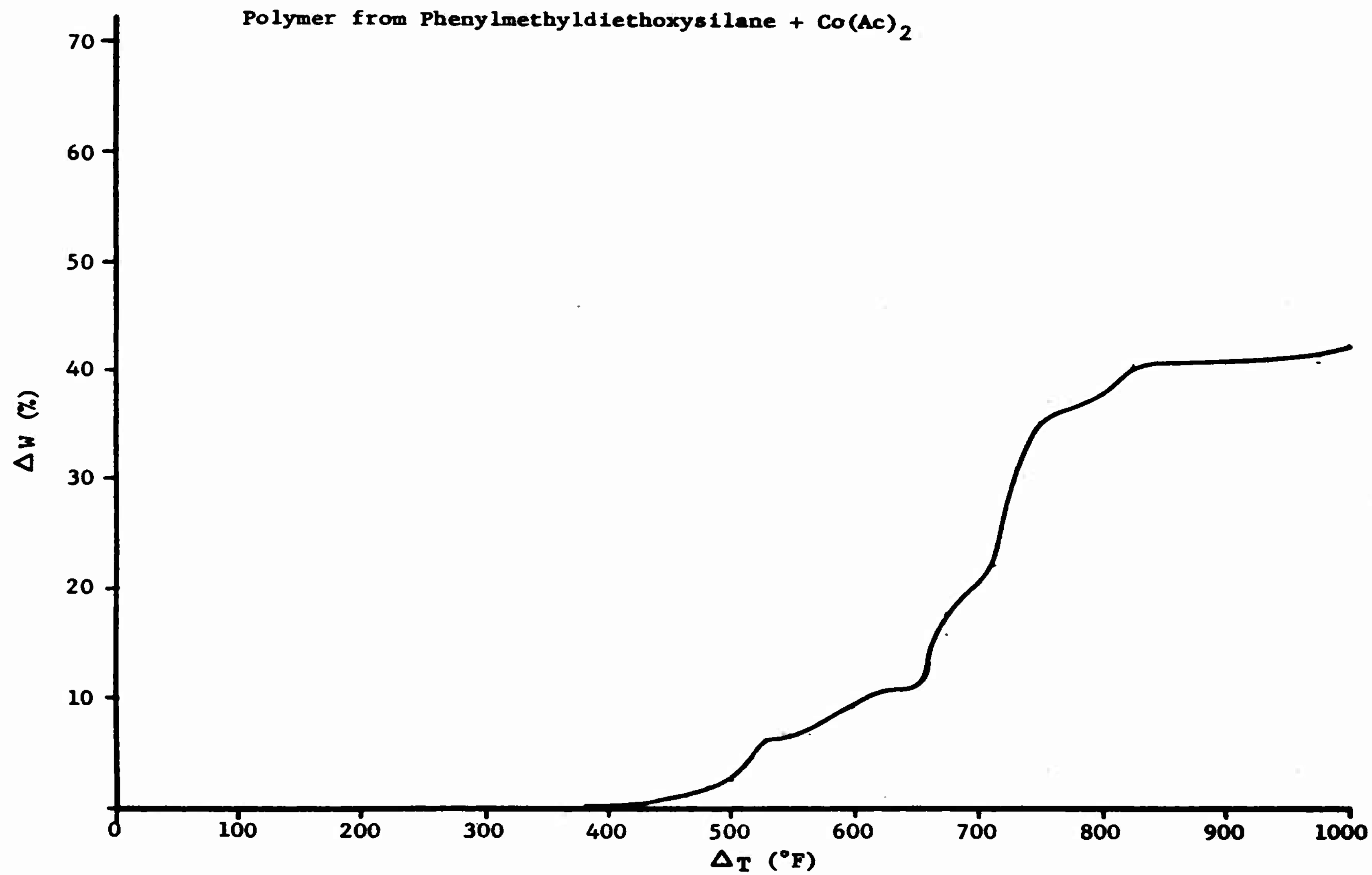


Figure 8

Polymer from Phenylmethyldiethoxysilane + $Co(Ac)_2$



EXPERIMENTAL

1. CONSTRUCTIVE PYROLYSIS

Laminates were prepared with the various resins on 181 E glass fabric with the recommended finish. The resin content was known for all laminates. After cutting into flexural specimens, two samples were weighed and put into the Vycor pyrolysis tube. After flushing with argon for an hour, the heat was applied and slowly raised to 1000°F. Temperatures were followed with a Wheelco potentiometer, using a chromel-alumel thermocouple. After some period of time, depending on the resin system, the tube was permitted to cool to 200°F before the argon was shut off. The specimens were weighed and the weight loss determined. One specimen was returned to the tube and the entire process repeated, except at 1800°F. The additional loss in weight was noted. The two pyrolyzed specimens, plus an untreated control whose weights were known, were subjected to either 650°F or 900°F in a circulating air oven. Periodic weighings were made to determine the loss in weight due to oxidation. Calculations of weight loss were based upon the amount of resin present after the respective treatments. See Tables I through VI.

2. ADHESIVES

a. Further work with Metlbond 309 was carried out to re-evaluate various polymeric oxides as metal primer and as a finish on the glass cloth carrier. The adhesive tapes were prepared in the usual manner, using 112-112 glass cloth as the carrier. Polymeric titanium dioxide was prepared by dipping either the cleaned steel or cloth in a 5% solution of tetra-isopropylorthotitanate in anhydrous benzene. On exposure to air, hydrolysis occurred to form the polymer. The proper technique was used if the film was blue, with rainbow colors, due to interference patterns. When the steel coupons were dipped, they were inverted when removed from the solution so that the solution would flow away from the bond area. In this manner, solution build-up would be avoided, thus preventing formation of white TiO_2 powder, which is detrimental to adhesion. See Tables I through VI.

b. A variety of B-staging conditions were used with the tapes and some changes in surface preparation carried out (polished vs unpolished steel prior to phosphate etch). All bonds were cured for two hours at 300°F, 75 psi, unless otherwise specified. See Tables VII through XIV.

c. The X-278 adhesive was prepared in the usual manner from an epoxy novolak, the #20 silicone-phenolic resin, arsenic sulfide and aluminum, and coated on 112-112 glass cloth. Curing conditions were the same as described in the second quarterly report. See Tables XV and XVI.

TABLE I

LOSS OF ORGANIC RESIN ON PYROLYSIS IN ARGON

Laminating Resin	% Wt. Loss 1000°F	% Wt. Loss 1800°F
Silicone-Phenolic #1	27.5	33.1
Silicone-Phenolic #2	29.4	35.3
Silicone on E glass	6.4	21.1
Silicone on Quartz	15.0	19.1
Epoxy Novolak	45.4	47.3
Phenolic	32.3	32.3
Epoxy	76.0	-

TABLE II

PYROLYZED SILICONE PHENOLIC LAMINATE
WEIGHT LOSS IN CIRCULATING AIR AT 650°F

Time hrs.	1000°F Pyrolysis % Change	1800°F Pyrolysis % Change	Control
2	-0.5	-0.5	-3.0
4	-7.0	-0.5	-4.5
6-1/2	-14.0	-0.5	-5.5
24	-59.0	-5.5	-16.5
30	-65.0	-6.5	-19.0

TABLE III

PYROLYZED SILICONE LAMINATE (E GLASS)
WEIGHT LOSS IN CIRCULATING AIR AT 900°F

Time hrs.	1000°F Pyrolysis % Change	1800°F Pyrolysis % Change	Control
1	-7.0	-0.4	-7.6
2	-10.0	-0.4	-10.1
3	-11.9	-0.5	-11.2
19	-29.9	-1.1	-19.6
27	-32.2	-1.3	-28.2
33	-34.5	-1.6	-31.8

TABLE IV

PYROLYZED SILICONE LAMINATE (QUARTZ)
WEIGHT LOSS IN CIRCULATING AIR AT 900°F

Time hrs.	1000°F Pyrolysis % Change	1800°F Pyrolysis % Change	Control
1	-18.4	-6.8	-6.9
3	-25.6	-12.0	-16.1
6	-29.4	-18.0	-20.0
30	-33.6	-29.4	-37.2

TABLE V

PYROLYZED EPOXY NOVOLAK LAMINATE
WEIGHT LOSS IN CIRCULATING AIR AT 650°F

Time hrs.	1000°F Pyrolysis % Change	1800°F Pyrolysis % Change	Control
1	+0.7	-0.5	-8.9
2	-1.8	-0.5	-12.4
4	-6.4	-0.5	-15.5
6	-9.5	-0.6	-17.2
22	-31.3	-2.3	-39.8
30	-35.8	-3.4	-51.4

TABLE VI

PYROLYZED PHENOLIC LAMINATE
WEIGHT LOSS IN CIRCULATING AIR AT 650°F

Time hrs.	1000°F Pyrolysis % Change	1800°F Pyrolysis % Change	Control
1	+2.2	-0.4	-3.8
3	-2.4	-0.4	-7.9
5	-11.0	-0.4	-12.4
10	-34.0	-1.5	-22.9
30	-76.0	-8.6	-51.0

TABLE VII

METLBOND 309 ON 17-7 STAINLESS STEEL

B Staged: 6 hours in vacuum oven, 10 minutes at 200°F, 5 minutes at 250°F.

Prime: TiO_2 on glass cloth. Steel Polished

Time mins.	Temp. °F	Average psi
2	1000	343
60	700	819
60	900	264
60	1000	413

TABLE VIII

METLBOND 309 ON 17-7 STAINLESS STEEL

B Staged: 6 hours in vacuum oven, 10 minutes at 200°F, 5 minutes at 250°F.

Prime TiO_2 on glass cloth and steel. Unpolished

Time mins.	Temp. °F	Average psi
2	1000	390
60	700	1157
60	900	547
60	1000	536

TABLE IX

METLBOND 309 ON 17-7 STAINLESS STEEL

B Staged: 7.5 hrs in vacuum oven, 5 minutes at 200°F.

Prime: TiO_2 on glass cloth and steel

Time mins.	Temp. °F	Average psi
-	R.T.	1816
2	1000	588
60	700	635
60	900	693
10	1000	716
30	1000	276
60	1000	381

TABLE X

METLBOND 309

B Staged: 7.5 hrs in vacuum oven, 5 minutes at 200°F.

Prime: None

Time mins.	Temp. °F	Average psi
-	R.T.	2330
2	1000	658
60	700	1597
60	900	913
10	1000	856
30	1000	476
60	1000	249

TABLE XI

METLBOND 309 ON 17-7 STAINLESS STEEL

B Staged: 30 minutes in vacuum oven at 200°F.

Prime: None. Steel Polished

Time mins.	Temp. °F	Average psi
2	1000	690
60	700	808
60	900	904
60	1000	0

TABLE XII

METLBOND 309

B Staged: 30 minutes in vacuum oven at 200°F.

Prime: None. Steel Unpolished

Time mins.	Temp. °F	Average psi
2	1000	688
60	700	1182
60	900	385
60	1000	96

TABLE XIII

METLBOND 309 ON 17-7 STAINLESS STEEL

B Staged: 6 hours in vaccum oven, 10 minutes at 200°F, 5 minutes at 250°F.

Prime: TiO_2 on glass cloth; SbO_2(1) on steel.

Time mins.	Temp. °F	Average psi
2	1000	551
60	700	1122
60	900	239
60	1000	100

(1) From hydrolysis "in situ" of 5% solution of isopropylantimonite.

TABLE XIV

METLBOND 309 ON 17-7 STAINLESS STEEL

B Staged: 6 hours in vacuum oven, 10 minutes at 200°F, 5 minutes at 250°F.

Prime: MgO(1) on glass cloth and steel

Time mins.	Temp. °F	Average psi
2	1000	213
60	700	176
60	900	258
60	1000	0

(1) From hydrolysis "in situ" of 5% solution of MgOMe.

TABLE XV

X-278 ON 17-7 STAINLESS STEEL

(Steel Not Polished)

Time mins.	Temp. °F	Average psi
2	1000	648
60	700	879
60	900	410
60	1000	0

TABLE XVI

X-278 ON 17-7 STAINLESS STEEL

(Steel Polished)

Time mins.	Temp. °F	Average psi
2	1000	492
60	700	762
60	900	402
60	1000	0

d. One batch of adhesive based on a phenolic was prepared, filled with aluminum and coated on 112-112 glass fabric. The tape was B-staged for 17 minutes at 180°F and used to bond stainless steel. These data are given in Table XVII, listed as X-282.

e. As part of the mechanism studies, dithio-oxamide was reacted with X-2638.1 epoxy-novolak in the ratio of 30:100 parts. The adhesive was applied to the steel and cured at 50 psi at room temperature to start flow, then 30 minutes at 200°F, 15 minutes at 225°F, 15 minutes at 250°F, 15 minutes at 300°F, and 2 hours at 350°F. See Table XVIII.

f. The same epoxy-novolak, X-2638.1, was reacted with zinc diethyldithiocarbamate. Two attempts ended in a destructive exotherm because of the reactivity of the zinc salt. The adhesive was finally prepared, applied to the 17-7 steel, and used the same way as the dithio-oxamide system. See Table XIX.

g. The X-278-A formulation was modified by substitution of the DEN 438 epoxy-novolak having a higher functionality than X-2638.1. The adhesive was put on 112-112 glass fabric, applied to the steel and cured for 2 hours at 600°F at 75 psi and cooled to room temperature in the press. The data are shown in Table XX.

h. The X-278-A adhesive was prepared and to this was added the extremely reactive stannic salt of 2-mercaptobenzothiazole (2% by wt.). Two sets of bonds were prepared, one cured at the usual 600°F, the other for two hours at 350°F. See Table XXI.

3. MECHANISM STUDIES

a. Phenylglycidylether and 10 Parts Thiourea

A 300 ml 3-necked flask was fitted with a long condenser, inner thermometer and mechanical stirrer and was charged with 100 g (0.667 mole) of phenylglycidyl ether. A total of 10.0 g (0.13 mole) of thiourea was added and the mixture heated and stirred at 150°C. The reaction became exothermic after 90 minutes; after cooling, the mixture was heated an additional 2-1/2 hours at 150°C.

Fractionation gave 3.68 g boiling at 56°C/4.5 mm, 3.28 g boiling at 76°C/2.0 mm. The dry-ice trap after the reaction contained two layers that were extracted with ether, and upon evaporation gave 1.12 g of product. All three materials gave negative carbonyl tests. Sodium fusions on the distillation residue gave a positive test for sulfur but was negative for nitrogen. However, heating the residue in strong sodium hydroxide gave vapors that were alkaline, indicating the presence of nitrogenous groups such as $-CONH_2-$, NH_2, NHR, NR_2.

TABLE XVII

X-282 ON 17-7 STAINLESS STEEL

Time mins.	Temp. °F	Average psi
-	R.T.	2640
60	700	1114
60	900	501
10	1000	873
30	1000	529
60	1000	275
2	1000	835

TABLE XVIII

X-2638.1 EPOXY NOVOLAK AND DITHIO-OXAMIDE
17-7 STAINLESS STEEL

Time mins.	Temp. °F	Average psi
-	R.T.	830
60	700	42
60	900	0
60	1000	0

TABLE XIX

X-2638.1 EPOXY NOVOLAK AND ZINC DIETHYLDITHIO-CARBOMATE
17-7 STAINLESS STEEL

Time hrs.	Temp. °F	Average psi
-	R.T.	3045
1/6	550	58
1	"	114
5	"	118
10	"	127
50	"	595
100	"	616
192	"	330
10 mins.	700	10
"	900	88
"	1000	8
1	700	58
"	900	0
"	1000	0
2 mins.	1000	50

TABLE XX

X-278-A WITH DEN 438 IN PLACE OF X-2638.1

Time mins.	Temp. °F	Average psi
2	1000	974
-	R.T.	1890
60	700	1095
60	900	684
60	1000	0
10	550	1013
50 hours	550	1120
192 hours	550	453

TABLE XXI

X-278-A PLUS 2% STANNIC 2-MERCAPTOBENZOTHIAZOLE

Time hrs.	Temp. °F	Average, psi	
		600°F Cure	350°F Cure
-	R.T.	1677	1404
1	700	986	650
1	900	692	428
1	1000	0	0
2 mins.	1000	847	402
10	550	993	423
50	550	610	641
192	550	204	433

The residue showed peaks at 2.9-3.2μ (hydroxyl and/or -NH), 5.8μ (carbonyl), and a weak peak at 7.35μ (C=S). The 5.8μ peak could be from a $-O\overset{O}{C}NH$. These absorptions were absent in phenylglycidylether. Epoxy absorptions present in the starting material were absent in the distillation residue.

Examination of the lower boiling fraction showed peaks at 2.9-3.2μ (OH and/or NH) and 7.4μ (C=S) which were absent in the epoxy compound. Both the higher boiling fraction and the trap condensate had a peak at 5.8μ (carbonyl). The higher boiling fraction had an absorption at 11.7μ which was absent in the trap condensate.

b. Phenylglycidylether and 30 Parts Thiourea

The same reaction was run as above. At 90°C, a violent exotherm occurred in which the temperature reached 240°C. After the exotherm subsided, the mixture was heated at 120°C for 3 hours and the contents dissolved in dioxane. On standing, a yellow viscous liquid and white crystals separated. After filtration, the crystals were recrystallized in dioxane to give a substance, m.p. 127-128°C. Mixed melting point with urea was 130-132°C; urea has a melting point of 130-132°C; infrared spectra also showed this to be identical with authentic urea. Infrared on the reaction product showed the changes mentioned above; in addition, an absorption at 6.05μ appeared, which could be due to either an amide or olefinic group.

c. Phenylblycidylether and 10% As_2S_3 in Nitrogen

This experiment was carried out to see if As_2S_3 formation was due to air oxidation of the sulfide at elevated temperatures. In all instances, the reaction was identical to the ones run in air, including IR spectra of all portions of the reaction mixture, arsenic trioxide was still found.

To determine the possibility of thioether linkages, some of the residue after distillation was dissolved in glacial acetic acid and heated in the presence of hydrogen peroxide. A new peak appeared at 8.9-8.95μ along with a shoulder at 7.65 μ; these are sulfone absorption assignments.

Fractional distillation of the reaction mixture gave phenol in the lower boiling fraction. The intermediate fraction had a peak at 9.03μ, which was absent in phenylglycidylether.

d. Diphenyldiethoxysilane and 10% As_2S_3

After heating for 2-1/2 hours up to 225°C, no signs of reaction were visible and the IR spectrum on the mixture was unchanged.

4. SYNTHESIS

a. Hycar 1042 and Hydroxylamine

Hycar 1042 (nitrile rubber) was made soluble in dimethylformamide by breaking down the molecular weight on a rubber mill. Ten grams of the rubber was dissolved in 2-liters of dimethylformamide and heated to reflux, with stirring. To this solution was added a mixture of 4.0 g finely powdered hydroxylamine hydrochloride and 3.0 g anhydrous sodium carbonate. After refluxing 3 hours, the solution was filtered and distilled "in vacuo" to remove 1 liter of solvent; the remaining solution was slowly poured into 1 liter of water to give a dark brown solid. A sample was dissolved in tetrahydrofuran for examination in the IR. A total of 6.1 g of crude polymer was obtained, which was also soluble in dioxane. The IR spectrum revealed a large decrease in $-C\equiv N$ absorption at 4.5μ and the appearance of a strong bond at 6.2-6.6μ, likely due to $-N=C$ linkages.

Solutions of copper, nickel and cobalt acetates were preapred in dioxane and added to the polymer dissolved in the same solvent. Only Ni^{++} gave a precipitate, which on drying was found to be heat sensitive.

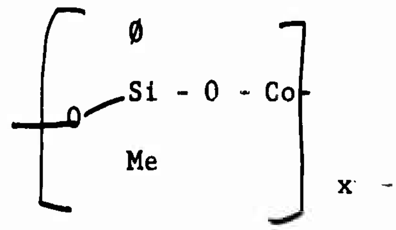
b. Phenylmethyldiethoxysilane and Cobalt Acetate

Cobalt acetate was heated at 150°F for 4 hours to remove water of crystallization.

A mixture of 50.0 g of the diethoxysilane and 35.9 g of the acetate was heated an stirred in a 3-necked flask provided with an inner thermometer, stirrer and a condenser set for distillation and a drying tube at the end of the receiver.

At 185°C, a distillate was collected, boiling at 70-76°C. After 1-1/2 hours the distillation temperature started to climb and the reaction stopped. A yield of 16.8 g of ethyl acetate was obtained, N_D^{25} 1.3780. The purple reaction solid was removed from the flask, washed with ether and dried to give a 21.4 g of product, m.p. 405°C, that burned on a spatula. Infrared analysis showed Si-O absorptions at 9.8-9.9μ and Si-Ø at 9.0-9.4μ, and 6.25-6.65μ. TGA gave a total weight loss of 42.1% up to 1000°F.

Since an excess of cobalt acetate was present, the material was boiled in water for 1/2 hour to remove this and also test hydrolytic stability. The solid so obtained was still organic in nature. Subsequent analysis showed 25.2% cobalt and 15.8% silicone and 40.0% organic material, thus indicating that the polymer was hydrolytically stable and had a composition close to the theoretical



Theory: Co 27.9%

Si 13.3%

Organic 43.6%

Analysis was carried cut by ignition to constant weight to obtain the organic content. The residue of Co_2O_3 and SiO_2 was treated with HF. The residue was then heated with sulfuric acid to form $Co_2(SO_4)_3$, and to remove all HF, which was ignited to Co_2O_3. All operations were carried out in a platinum crucible.

c. XR-820 and Cobalt Acetate

This triphenyl pentaethoxytrisiloxane was reacted with cobalt acetate as above, but with a large excess of the silicone compound. When completed, a total of 7.7 g of ethyl acetate and 9.5 g of crude solid were obtained. The solid was found to contain 19.8% Co and 10.6% Si while theory required 19.2% and 11.7% respectively. TGA analysis showed very little difference in total weight loss, except the major slope occurred at 100°F lower temperature than the polymer from phenylmethyldiethoxy silane.

d. p-Phenylene Diarsonic Acid

The method followed was that received from Dr. T. P. Hobin of Great Britain at the suggestion of Dr. Porter W. Erickson.

109 g of p-arsanilic acid was dissolved in 250 ml H_2O containing 101 ml concentrated HCl. Crushed ice was added to make the total volume up to 750 ml. To this solution was added, beneath the surface, a solution of 36.5 g $NaNO_2$ in 125 ml H_2O. The temperature of the mixture was held between 0-5°C during the addition.

125 g of anhydrous Na_2CO_3 was dissolved in 250 ml of boiling water. 62.5 g As_2O_3 and 3 g $CuSO_4$ were then added to the solution. An additional carbonate solution was made up containing 53 g anhydrous Na_2CO_3 in 250 ml H_2O.

The arsenite solution was cooled to 0°. The ice-cold diazonium chloride solution then added, beneath the surface, to the arsenite solution. The carbonate solution was added to the arsenite solution concurrently. Additional base (NaOH) was added to maintain the alkalinity of the arsenite solution.

After all the reactants had been added, the mixture was stirred for one hour at 5°C.

Work Up - The mixture was heated to 90-95° with stirring. Activated carbon was added and the mixture filtered while hot. The resulting solution is clear, dark brown.

This solution was then concentrated under vacuum to approximately one liter. The dark brown solution was then acidified slowly with stirring until an appreciable amount of light-colored precipiate had formed (pH 5-6- 200 ml of concentrated HCl added).

This was filtered, yielding a light-brown solid and a dark filtrate which was further acidified and filtered after each addition. Yield 108 g (65%) m.p.$>$ 405°C.

e. Polymerization of Benzyl Alcohol

The procedure followed was that of R. L. Shriner and A. Birger, J. Org. Chem. Vol. 6, 305 (1941).

Two hundred fifty ml. of concentrated H_2SO_4 was cooled to 0-3°C, and 43.5 ml (45.2 g) of benzyl alcohol was added very slowly to the acid. The reaction was highly exothermic. The temperature was maintained below 10°C. A red precipitate formed immediately. After addition of the benzyl alcohol was completed, the mixture was poured into a beaker of cracked ice. The resulting cream-colored precipitate was filtered, washed, and then dissolved in dioxane.

A portion of the material was insoluble in dioxane. After filtering and repeated washings with H_2O, this portion yielded a light tan powder, m.p. 56-63°C, yield 27.7 g.

The dioxane filtrate, containing the soluble portion of the polybenzyl, was diluted with H_2O. No precipitate formed.

f. Oxidation of the Polybenzyl to a Polyketone

Five grams of the powdered polybenzyl polymer was placed in a 1000 ml flask with a mixture of 100 ml concentrated HNO_3 and 400 ml H_2O. The mixture was then refluxed. After two hours the yellow-organge crust that formed was pulverized and then refluxed for four more hours with a fresh acid solution. The solid formed was then pulverized and washed repeatedly with H_2O, m.p. 120-130°C, yield 5.1 g.

An infrared spectrum of the compound had peaks that could be associated with a diaryl ketone or a carboxylic acid.

One gram of the material was washed with a 10% Na_2CO_3 solution. After washing and drying, there was no change in the m.p., but an IR did show reduced OH with the carbonyl remaining the same.

g. An attempt was made to use the diarsonic acid as a curing agent.

Five g of DEN 2638.1 resin and one g of the diarsonic acid were mixed together in an aluminum cup and heated on a hot plate with occasional stirring. The mixture was heated at the following times and temperatures successively:

230°F - 1-1/2 hours
350°F - 1 hour
425°F - 1 hour
320°F - 1 hour

No visible change occurred at any time. The acid did not dissolve in the resin. An IR showed no change from the starting mixture.

h. Diphenylsilanediol and Aluminum

60 g. of the silane, 2 g of aluminum powder, and 15 mg of $HgCl_2$ were mixed together in a 1000 ml beaker and heated with stirring. The silane melted at 80-85°C. After one hour, the temperature was at 175°C. The aluminum had not dissolved and the viscosity had increased.

At 1-3/4 hours, the mixture became exothermic from 210° to 245°C, but the aluminum had apparently not dissolved. The reaction was stopped after two hours with the temperature at 220°C. The residue was a grey, brittle solid at room temperature. It softened about 200°F.

Some of the residue was powdered and dissolved in benzene. The aluminum powder settled out quickly, but there was a small amount of a gelatinous precipitate that settled slowly. A small amount of the material was isolated by evaporating the solvent. An IR of this was inconclusive.

i. Trichloroborazole and Glycidol

To 2.4 g of B,B',B" trichloroborazole dissolved in 25 ml of anhydrous CCl_4 placed in a 100 ml flask fitted with a stirrer, dropping funnel, thermometer, and capillary tube for bubbling N_2 through the reaction mixture, was added 2.9 g of glycidol dissolved in 20 ml CCl_4. This was added slowly to the borazole solution under a nitrogen atmosphere.

A white precipitate formed almost immediately. There was a mild exotherm (temperature up to 35°C). The mixture was stirred for one hour at room temperature after the addition was completed.

After standing overnight, the white precipitate was floating on the CCl_4. The precipitate was filtered off and dried under vacuum. The compound was very hygroscopic. The CCl_4 was evaporated from a sample of the filtrate on a NaCl crystal. The IR spectrum had a strong OH absorption.

A Nujol mull of the white solid was unsatisfactory because some important areas were obscured. It was impossible to run the powder alone because of its hygroscopic nature, m.p. 85-90° (decomposes). A water solution of the solid has a pH of 8-9 and gives a positive chloride test.

Burning some of the product resulted in the following: melted with bubbling and smoking (smoke has a pH 8-9 and its odor resembles burning epoxy resin) followed by burning, first with green flame (boron) then yellow, then a black, carbonaceous appearing residue remained (about 1/3 the original amount).

j. Zinc Salt of 2-Mercaptobenzothiozole

In a 300 ml 3-necked round bottom flask was placed a freshly prepared solution of 11.53 g (0.075 mole) of 2-mercaptobenzothiozole and 3.0 g (0.075 mole) of NaOH in 100 ml of water. While the solution was stirred at room temperature, 5.10 g (0.0375 mole) of $ZnCl_2$ in 100 ml of water was added. After the dropwise addition of the $ZnCl_2$ was completed, stirring was continued for 1 more hour. An almost white precipiate formed that was separated from the mother liquour by suction filtration, was washed twice with EtOH and dried in air. Yield 14.0 g.

k. Antimony-2-Mercaptobenzothiozole

11.53 g (0.075 mole) 2-mercaptobenzothiozole was stirred in a 100 ml of CCl_4 in a 200 ml 3-necked round bottom flask fitted with a reflux condenser, stirrer and dropping funnel. The mixture was refluxed for 30 minutes and then 3.89 g (0.015 mole) of $SbCl_5$ was added dropwise with stirring. A precipitate formed that was brownish in color. It was filtered by suction, washed first with water, then with EtOH, and dried in air. Yield 12.4 g.

l. Tin-Salt of 2-Mercaptobenzothiozole

In a 200 ml 3-necked round bottom flask fitted with a dropping funnel, stirrer and reflux condenser connected to a drying tube, was placed a solution of 11.53 g (0.075 mole) of the mercaptan in 100 ml of CCl_4. The solution was kept under reflux and 4.68 g (0.018 mole) of $SnCl_4$ was added dropwise with stirring. A bright yellow precipiate formed and was washed with water, then EtOH, and dried in air. Yield 13.5 g.

CONCLUSIONS AND RECOMMENDATIONS

1. CONSTRUCTIVE PYROLYSIS

   a. Regardless of the commercial laminating resin used, E glass laminates pyrolyzed at 1800°F in argon gained significantly in oxidation resistance.

   b. In all cases but one, pyrolysis at 1000°F in argon resulted in very poor oxidation resistance, even poorer than the unpyrolyzed control.

   c. Pyrolysis of E glass laminates resulted in low resistivity.

   d. A silicone laminate on quartz fabric performed much more poorly than the corresponding E glass laminate.

   e. The resistivity of the quartz laminate was almost infinite.

   f. Pyrolysis of E glass laminates containing silicone or silicone-phenolic resins resulted in some fusion of the glass; this was absent in laminates made from non-silicone containing resins.

   g. The low resistivity of silicone-E glass laminates and very high resistivity of silicone-quartz laminates appears to be due to a reaction with the E glass which contains aluminum, calcium and boron oxides, which could give rise to ionic species.

   h. Degradation of E glass on protracted exposure at elevated temperature was absent in the specimen pyrolyzed at 1800°F.

2. ADHESIVES

   a. Substitution of DEN 438 for X-2638.1 in the X-278-A adhesive gave improvement in tensile shear after 192 hours at 550°F.

   b. The modified X-278-A system gave almost 900 psi after 2 minutes at 1000°F, using a rapid heat up cycle.

   c. Surface priming and finishing on glass with various polymeric oxides were either of no benefit or detracted from performance.

3. MECHANISMS

   a. The reaction of arsenic trisulfide with epoxy compounds is very complex.

b. Phenylglycidyl ether and arsenic trisulfide gave phenol, a very small amount of an unknown carbonyl compound suspected to be acrolein and primarily polymeric materials.

c. There are indications, still unsubtantiated, that there is an oxygen-sulfur exchange to form arsenic trioxide and a thiirane compound. The thiirane compound then polymerizes to form a polymeric thioether.

d. The type of polymerization of the epoxy, either to a polyether or a polyhydroxy compound, seems to vary, depending on the sulfur compound and epoxy compound used.

e. In a similar fashion, thiourea and dialkyldithiocarbamates, on reaction with phenylglycidyl ether, gave infrared spectra that contain amide absorptions, indicating replacement of sulfur by oxygen.

4. SYNTHESIS

a. Reaction of cobalt acetate with alkoxy silanes gave polymers containing the Si-O-Co- linkages.

b. Such polymers appear to be hydrolytically stable.

c. The synthesis of p-phenylene diarsonic acid was accomplished.

d. Reaction of stannic chloride with 2-mercaptobenzothiazole apparently failed to yield the desired stannic mercaptide, but instead gave the Lewis salt by coordination with the ring nitrogen atom.

FUTURE WORK

1. CONSTRUCTIVE PYROLYSIS

   a. Pyrolysis of silicone and silicone-phenolic laminates on asbestos will be carried out to compare oxidation resistance, physical strength retention and resistivity.

   b. Pyrolysis of tensile shear specimens will be attempted.

   c. The possibility of reaction between a silicone resin and E glass will be investigated.

2. ADHESIVES

   a. The use of DEN 438 will be evaluated more thoroughly for use in X-278-A adhesives.

   b. Some work will begin to investigate various fillers as replacement of aluminum.

   c. Attempts to improve Metlbond 309 and X-282 will also continue.

3. MECHANISMS

   a. The reaction of arsenic trisulfide with epoxy compounds will be extended to other epoxy compounds with simpler infrared spectra to make detection of changes more readily apparent.

   b. Attempts to demonstrate a thioether linkage will continue.

4. SYNTHESIS

   a. The cobalt acetate reaction will be extended to attempt the preparation of a cobalt modified #20 silicone-phenolic resin for use in X-278-A adhesive.

   b. The use of other metallic acetates will be attempted.

   c. Reactions of the diarsonic acid with epoxy and phenolic compounds will be tried.

   d. Attempts to synthesize resins with lower organic content will be carried out by reaction of a polysilicate with Bisphenol-A and cobalt acetate.

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